Thermal evolution of cluster assembled Ni₃Al materials modelled at the atomic scale

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Abstract. Diffusion properties of Ni₃Al cluster assembled nanostructured materials are investigated at the atomic scale. Two different model samples are considered, at equilibrium at 300 K. One is obtained by modelling cluster compaction under 2 GPa external pressure and the second by accumulating low energy deposited clusters on a Ni surface. They differ essentially by their density, the latter sample presenting an interconnected network of nanopores, which is not observed in the former. At elevated temperatures, cluster coalescence is observed in both, as well as an intense atomic diffusion at the internal surfaces and nanograin interfaces. A method is presented which allows, in a good approximation, to distinguish between the two phenomena and to estimate diffusion coefficients. At temperatures above 400 K, it is found for both samples, irrespective to their density, that the diffusion activation energy at the internal surfaces and interfaces is as low as in a liquid while the grain cores remain crystalline.

PACS. 61.43.Bn Structural modeling: serial-addition models, computer simulation – 36.40.-c Atomic and molecular clusters – 61.46.+w Nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals

1 Introduction

Bi-metallic nanoparticles are at the origin of several technological challenges involving catalytic, optical, magnetic and electronic applications. Isolated particles have properties specific to the nanosize and an important question is to identify to which extent their properties may be retained when assembling them to form a bulk nanostructured material. A corollary question is to identify possible properties of such new materials and this is the frame of the present work. One significant finding in this direction is superplasticity, experimentally evidenced in nanostructured materials [1], which stimulated the question of interfacial state and mechanical deformation. Since one decade, interfacial states and deformation mechanisms are subjected to substantial studies [1–8]. Bulk properties of nanostructured materials depend on the synthesis method and we focus here on systems formed by nanoparticles as building blocks. Starting with nanoparticles, bulk nanostructured materials may be synthetised by assembling them from the gas phase by inert gas condensation followed by compaction or by low energy deposition on a substrate surface. One obvious question is the role of the synthesis itself on the modification of the nanoparticle properties. The capillary pressure in an isolated particle may be quite high and was estimated theoretically of the order of 2 GPa typically, in metallic particles of the order of 2 to 10 nm diameter [9]. A possible consequence in a bi-metallic particle is an enhanced surface segregation of one of the species, as predicted by atomic scale modelling [10]. It comes out modelling that this pressure, induced by the presence of free surfaces is replaced by interfacial stress when the nanoparticles are assembled. The interfacial segregation state is predicted closely similar to that of the isolated clusters [11]. In case of particle deposition modelling shows that the particle-surface interaction may have important consequences, depending upon the deposition energy [12,13] and the nature of the substrate [13,15]. Profound atomic rearrangement is possible in the particle [14,16,17] characterised by a competition between chemical and structural ordering in case of bi-metallic particles [11,15]. Nevertheless, modelling predicts that the structural and thermodynamic properties of the nanoparticles are generally retrieved to a large extent after assembling. As temperature is concerned, it was predicted in [15] that it influences the competition between structural and chemical order at the vicinity of the interface with a substrate during low energy cluster beam deposition. In the present work, we investigate the role of elevated temperature on the nanostructure of films formed both by bi-metallic clusters under deposition and by inert gas condensation followed by compaction.

The paper is organised as follows: Section 2 briefly describes the cohesion model and the Molecular Dynamics
(MD) simulation methods used and the characteristics of the model sample used [11] are briefly described. Section 3 is devoted to a qualitative description of the thermal evolution of model samples at elevated temperature and their diffusive properties. In Section 4, a quantitative method for distinguishing between coalescence and diffusion and determining the diffusion coefficients is presented. The obtained results are discussed. The main conclusions are summarised in Section 5.

2 The simulation model and the model samples

The purpose of this work is to study the thermal evolution of nanostructured samples that were synthesised. The building blocks are Ni₃Al clusters initially modelled as isolated systems containing from a few hundred to a few thousand atoms each [10]. Their thermodynamic equilibrium state in a temperature range from 100 K to 700 K was predicted by Metropolis Monte Carlo modelling (MC) in the semi-grand canonical ensemble [18]. Their assembling at room temperature was then modelled by Molecular Dynamics (MD) with two different models appropriate for modelling the compaction after inert gas condensation and the other for modelling their accumulation by low energy cluster beam deposition [11]. MC simulation starting from the obtained nanostructured model samples allowed finding their new thermodynamic equilibrium state. The study of their thermal evolution at temperatures above 300 K is reported in the present paper.

2.1 The simulation model

A thermal vibration period in a solid is of the order of the picosecond. Since MD allows to study the evolution of a system of the size of our nanostructured samples (twenty to fifty thousand atoms) for times of the order of the nanosecond or more, it is a well suited technique for studying their thermal evolution. Since the two MD techniques employed were already described in previous papers, the models will only be briefly outlined here.

The basic parameter of MD is the interatomic potential describing the interaction between atoms. A many-body potential has been used based on the second moment approximation of the electronic density distribution [19,20] as derived from the tight-binding (TB) theory for transition metals. According to this model, the cohesive energy projected onto one atom can be written as

\[ E_i = F(\rho_i) + \frac{1}{2} \sum_{j \neq i} \varphi(r_{ij}) \]  

where \( F(\rho_i) \) is a function of the electronic density \( \rho_i \) at site \( i \) and \( \varphi(r_{ij}) \) is the pairwise contribution of the repulsive energy between atoms \( i \) and \( j \) separated by the distance \( r_{ij} \). The electronic density \( \rho_i \) at the site \( i \) is expressed as a functional of pairwise contributions. It may be written as

\[ \rho_i = f \left( \sum_{j \neq i} \Phi(r_{ij}) \right). \]

In the second moment TB approximation, this functional is a square root. The total cohesive energy of the system is

\[ E_T = \sum_{i=1}^{N} E_i. \]

The functionals \( \varphi \) and \( F \) are adjusted semi-empirically and we use the parameterisation in [21–23]. In this expression \( \varphi(r_{ij}) \) and \( \Phi(r_{ij}) \) are approximated by a set of cubic splines which parameters are used to fit the potential to the cohesive energy, the equilibrium condition and the elastic constants. A cut-off distance equal to 1.225\( a_0 \), where \( a_0 \) is the lattice parameter, limits the range of the local interactions.

In its simplest form, MD merely consists in numerically solving a system of coupled Newton equations of motion in the microcanonical (NVE) statistical ensemble for the particles contained in the simulated box [24,25]. In systems like nanostructured materials, which are characterised by deep inhomogeneities, it is possible to account for the dynamics of the macroscopic anisotropic deformation of the simulation box, at constant external pressure and temperature. This is achieved in the canonical ensemble according to the constrained MD scheme by Rahman and Parrinello (RP-MD) [26,27]. In this scheme, the simulations are performed in the (NPT) ensemble and the system is coupled to a thermal bath by means of the scheme proposed by Nosé [28]. It is not possible to use the RP-MD scheme without further constrains for a system having free surfaces. This is no problem for systems formed by compaction, for which periodic boundary conditions may be applied in three different directions to mimic an infinite system. On the contrary, a nanostructured film formed by cluster beam deposition necessarily has a surface. In addition, it is constrained by the substrate at the interface. Therefore, (NVT) simulations were used in this case. Here, the temperature is also constrained by a thermal bath. The method used however differs from the Nosé scheme in the sense that the Nosé bath is supposed to be the electronic system and the exchange of heat is governed by the electron-phonon coupling (see [13] for further detail). Constant volume is insured by periodic boundary conditions applied to the simulation box and the whole system (including the deposited layer and the substrate upon which it is deposited) is constrained at the same constant temperature.

2.2 The model samples

Free Ni₃Al clusters at thermal equilibrium were prepared by Metropolis Monte Carlo and the method is explained in [10]. It was found that at 700 K and below, isolated equilibrium Ni₃Al clusters containing more than 200 atoms may crystallise and are partitioned into two areas; a core